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A Bespoke Contact Angle Measurement Software and Experimental Setup for Determination of Surface Tension

Chin Fhong Soon[a,]*, Wan Ibtisam Wan Omar[a], Nafarizal Nayan[a], Hatijah Basri[c], Martha Bt. Narawi[b], Kian Sek Tee[b]

[a]*Biosensor and Bioengineering Laboratory, Microelectronics and Nanotechnology-Shamsuddin Research Center (MiNT-SRC), Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia.*

[b]*Faculty of Electrical and Electronic Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia.*

[c]*Faculty of Science, Technology and Human Development, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia.*

Abstract

Contact angle measurement has wide application in studying the wettability of a surface. This paper presents a contact angle measurement system developed using simple apparatus. The system consists of a bespoke measurement software, USB microscope, motorized linear position slider and a sample holder with back lighting system. The advantages of this system include user friendly, compact size, allow manual and automatic measurements and cost effective. This system is established with the contact angle and surface tension measurement experiment which is based on Fox-Zisman theory. Different probe liquids were suggested and the critical surface tension of polydimethylsiloxane (PDMS) and polyimide were determined using both the software and the hardware system developed.

Selection and peer-review under responsibility of the Faculty of Information Science & Technology, Universiti Kebangsaan Malaysia.

Keywords: Surface tension; contact angle measurent software; PDMS; polyimide

* Corresponding author. Tel.: +607-4538614; fax: +607-4536060.
E-mail address: soon@uthm.edu.my

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1. Introduction

The study of surface tension has wide application in applied surface science. Surface tension is related to the surface energy of a surface and it is determined by determining the contact angle of a sessile drop of liquid on a solid surface. Contact angle is measured by fitting a mathematical expression to the shape of the drop and then calculating the slope of tangent to the drop at the liquid-solid-vapor (LSV) interface line [1]. The interfacial tension of liquid-solid is related to the surface tension of the liquid and vapors at the interface by Young's relation. This relation that establishes the mechanical equilibrium between several surface tensions (Fig. 1) is:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos\theta \tag{1}$$

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \tag{2}$$

where s is for solid, l is for liquid, v is for vapour, and θ is the contact angle. Among the parameters, $\gamma_{lv}$and cos θ can be determined from the experiment. A contact angle (θ) is the interior angle formed by the substrate being used and the tangent to the drop interface at the apparent intersection of the three phase boundary (solid, liquid and vapour). The equation (Eq. 1-2) and the measured value of the contact angle are used as basis for calculating the surface energy [2]. This intersection is called the contact line. A static contact angle on a flat surface is defined by the Young's Equation which relates interfacial surface tensions between solid and liquid, γ_{sl}, solid and vapor, γ_{sv} and liquid and vapor, γ_{lv}. Young's equation is essentially a force balance in the horizontal direction of a surface. Fox-Zisman method is used to determine the critical surface free energy (γ_c). According to Zisman, the value of γ_c of a solid is equal the value of γ_l of a liquid being in contact with this solid and for which the contact angle is zero [2]. Based on the theory, γ_c value consists of the contact angle measurements for the studied solid and liquids of a homologous series of compounds. Then the plot is constructed in a coordination system with the y-axis corresponding to the cosine values of the contact angle and the x-axis relating to the surface tension of different probe liquids.

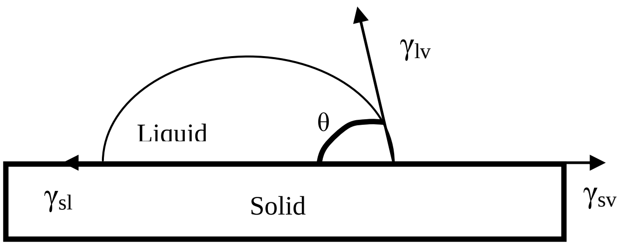

Fig. 1. Equilibrium of a liquid with a solid surface.

Contact angle measurements of a solid surface can be materialized using a simple approach as presented in [1]. However, in the previous system, the simplified apparatus requires the use of a separate lens and the back light system consists of a light bulb. The lens was used to magnify the captured image to an ordinary digital camera. The contact angle measurement was analysed off-line. The presented system is cumbersome and this paper aims to develop an improved system with more functionalities.

2. Materials and Methods

The contact angle measurements system presents in this paper was developed using up-to-date technology. This system consists of a stepper motor controlled microscope holder which was fixed with a USB microscope (Figure 2). The microscope holder attached to a motorised linear slider was used to adjust the right viewing angle between the microscope and the sample measurement stage (glass slide from Agar Scientific). A bespoke image acquisition and measurement software (CA measure tool) was incorporated to import the acquired video from the USB microscope. The contact angle measurements made in the software will be recorded and a Fox-zisman plot can be generated by the software. In addition, the USB microscope used has zoom function which magnifies images from 25x up to 200x. The linear slider which functions to position the USB microscope was scavenged from an old laser jet printer. An Arduino-uno controller and MOSFET current driver circuit (1A) were used to control the linear positioning of the stepper motor as shown in Fig.3. In order to increase the contrast of the imaging, a light emitting diode (LED) array working as back lights was added at the rear of the measurement stage.

The CA measure tool software was built in the MATLAB integrated development environment as shown in Fig. 4. In the software, the user can open a real-time video acquired by the USB microscope, snap an image and save the image in common graphic format such as *.tiff, *.jpg and *.bmp. To conduct the measurement of the contact angle of a droplet of fluid, one needs to first load the image by activating the load button in the CA measure tool. Subsequently, the user needs to calibrate the scale of the image if the user is interested to measure the length of the sample. However, the measurement of the angle can be done without the calibration process and the software could calculate the angle based on the pixel size of dimensions. After an image is loaded and the calibration is done, the user needs to define the contact angle by drawing two lines originating from the intersection point of a contact angle as shown in Fig.5. Alternatively, the software includes an automatic measurement algorithm which first crop the image of the droplet of solution and the user is required to enter the coordinates of the image cropped. After the image is cropped, the "Auto" button can be activated to allow automatic determination of the contact angle. In the "Auto" algorithm, the cropped image was turned into black and white image to outline the boundary of the droplet and the base line. The program was written to identify the base line coordinates and the apex of the droplet. From the apex, the algorithm traced down the boundary of the curvature "counter clockwise" using the *bwtraceboundary* and *polyfit* functions available in MATLAB. The base line of the substrate was found by determining the coordinates where the black and white transition occurred. From the coordinate of the base line the base line equation can be formulated. The intersection point of the boundary and the base line can be computed using the *polyxpoly* function. By determining, the intersection point of the two poly lines, the tangent line of the boundary of the droplet can be traced. The dot product of the tangent and base lines and the vector conversion provides the data needed to approximate the contact angle of the droplet automatically. Manual Angle Tool and Auto Angle Tool are two choices of manual and automatic angle measurement functions included in the CA measure tool.

In the validation experiment for the contact angle measurement system, a film of cured PDMS was prepared by mixing 10:1 ratio of elastomer and curing agent (Slygard, Corning). The film was cured in in an oven at 60^{o}C for 30 minutes. After curing, the PDMS film with a thickness of 2 mm was cut and placed on measurement stage. Subsequently, the acquisition and measurement of the contact angle image was taken based on the procedure described. In order to apply Fox-zisman's method in determining the surface tension, eight probe liquids as listed in Table 2 were selected for the experiment. They were in turn deposited on to the surface of the PDMS at randomly selected area using a syringe (Fig. 6) and 30 seconds equilibrium time was given for each probe liquids after each deposition. Each measurement was repeated 3 times. Similar experiments were repeated for polyimide film (80 µm thick) which was obtained from ebay.com.

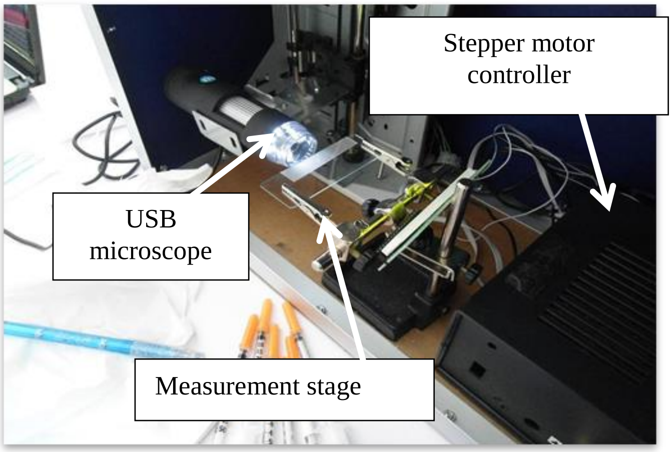

Fig. 2. Setup for the measurement apparatus and contact angle measurement software.

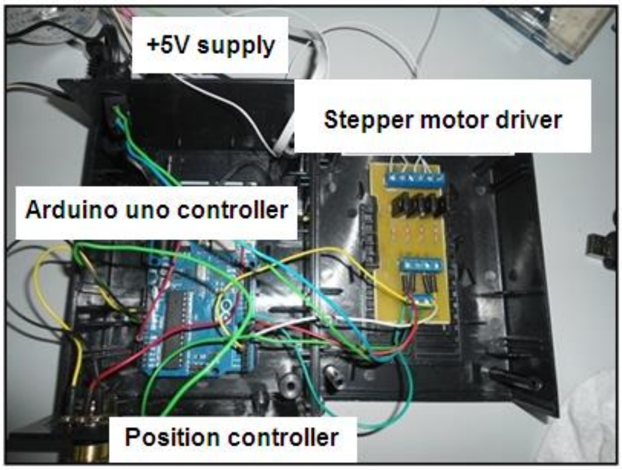

Fig. 3. Stepper motor controller circuit.

When the line drawing defining the angle of the droplet was done, the value of the angle will be displayed both on the image and in the status box of the CA measure tool (Fig. 4). The contact angle for the probe fluid will be recorded and the subsequent measurement process can be repeated for other probe liquids according to the sequence of the probe liquid arranged in Table 1. CA measure tool software allows contact angle measurements for 8 probe liquids and finally the linear regression line of the Fox-zisman plot can be produced. The result of the critical surface tension measurement will be computed and displayed in the status box. If the user made a mistake during the measurement of the contact angle, the value of the measurement can be deleted or re-edited using the functions available in the List and Delete buttons. The result in the listing can also be analyzed in the Microsoft Excel separately.

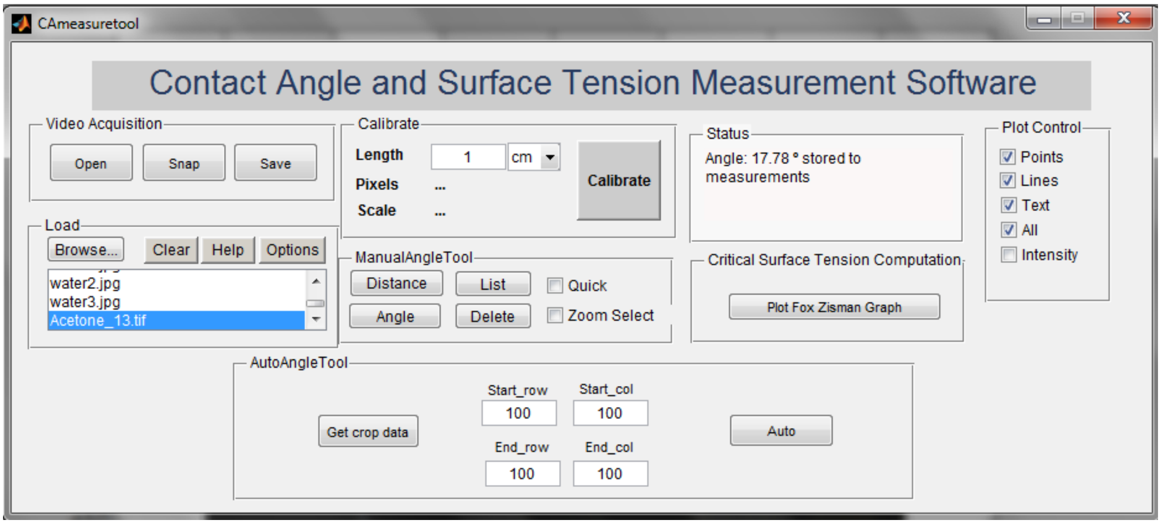

Fig. 4. Contact angle measurement software (CA measure tool).

Table 1. Probe liquids and its interfacial tension value.

Liquid	*Interfacial tension (mN/m)*
Isopropyl alcohol (IPA)	21.79
Acetone	23
Methyl-methacrylate (MMA)	30.6
Mineral oil	35
Dimethyl sulfoxide (DMSO)	42.90
Ethylene glycol (EG)	47.3
Glycerol	64
Distilled water	72.8

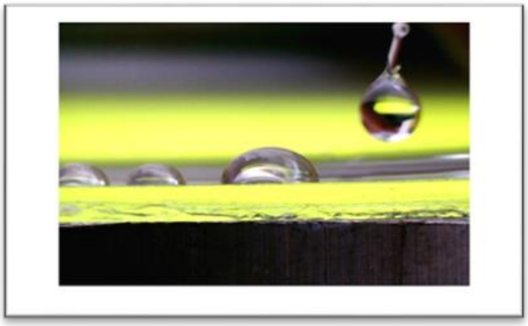

Fig. 5. Depositing probe liquids on a PDMS film sample under measurement.

3. Results and Discussion

Fig. 6 (a) shows the enlarged images of boundaries of a droplet placed on a substrate and the angles measurements produced by manual and automatic measurements. Although, manual mouse controlled measurement as shown in Fig. 6(a) provides the convenience in measuring and modifying an angle but it is subjective to the user who does the measurement. The choice of the intersection point and two poly lines locations with respect to the pixel intensity greatly affects the angle measurement as large as 20% difference. To improve the accuracy of measurement, the manual measurement should be performed with enlarged image (Fig. 6(a)) and this provided better approximation of the boundary line and base lines. In contrast, automatic measurement of contact angle depends on the base line and boundary detection (interpolated green polyfit line in Fig. 6(b)) which gives higher consistency in measurement. The shorter the tangent line with respect to the poly fitted curve approximates the actual tangent line of the curve better. In the same enlarged images, angle measurement produced manually and automatically produced similar values of measurements (Fig. 6).

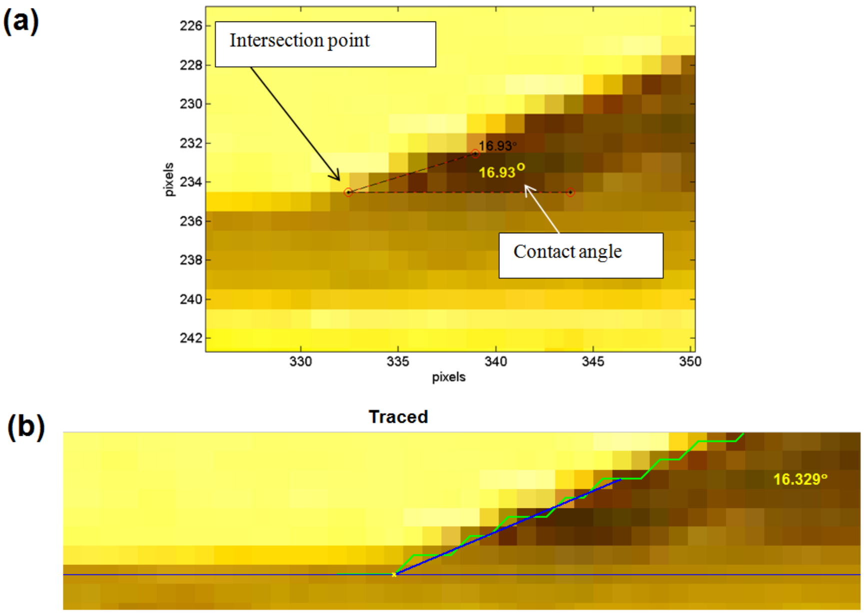

Fig. 6. Comparison of manual and automatic measurement of contact angles using (a) mouse control (Manual Angle Tool); (b) Polyxpoly function (Auto Angle Tool). Green and blue slope lines show the poly fitted boundary and tangent line approximated.

In validating the effectives of the entire system for determining the critical surface tension of the samples, Polydimethylsiloxane (PDMS) with well-established surface tension 19mN/m and Polyimide with surface tension 40mN/m were chosen for the validation study. Eight different probe liquids were selected for this project to determine the contact angle formed between these eight liquids and the surface of polymer under test. According to Fox Zisman's theory, selecting the suitable probe liquids is an important part of any contact angle measurement. A liquid can be considered a viable probe liquid for a dynamic contact angle experiment if it does not swell or react with the solid surface [3]. A good way to evaluate the appropriateness of a probe liquid is to deposit a drop of the liquid onto the surface and observe what happens to the droplet. If it is immediately absorbed into the solid, or completely spreads out across the surface, this liquid should be eliminated. Table 1 shows the probe liquids used in the experiment [3].

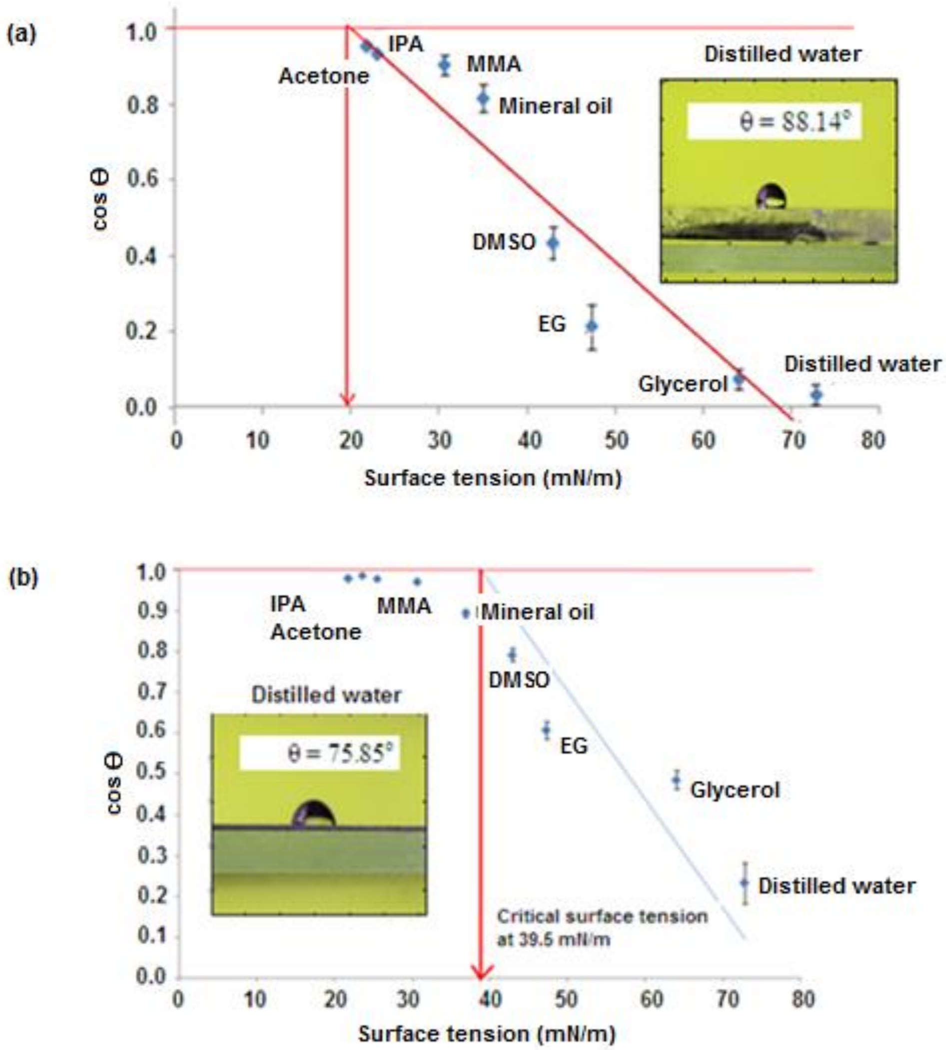

Fig. 7. Fox-zisman plots for (a) PDMS; (b) Polyimide films. The red arrows indicate the critical surface tension of PDMS and polyimide, respectively. Inset: Droplets of distilled water on the PDMS and polyimide surface.

The CA measure tool was used to capture the image of a sessile droplet of probe liquid on the surface of PDMS and polyimide films. From the image, it was observed that each of these liquids has their own fluid surface tension and therefore, formed different contact angles with the PDMS and Polyimide. In this experiment, we found that the contact angle of sessile drop is similar regardless of the droplet volume and this can be observed in Fig. 5. The equilibrium contact angle is specific for any given system and is determined by the molecular interactions across the liquid/vapor, solid/vapor and solid/liquid interfaces. According to the Fox-zisman theory, the critical surface tension corresponds to the minimum value of the liquid surface tension data set which is also crossing with the extrapolation of the best fitted regression line at cos θ =1 [4-5]. This value allows complete spreading of the liquid on the surface. As shown in Fig. 7, contact angle formed on the PDMS and polyimide film in association with the liquid surface tensions were plotted in a Fox-Zisman graph, in which, the critical surface tension of the

PDMS and polyimide surfaces was determined at 19.1 mN/m and 39.5mN/m, respectively. These values are in good agreement with the results published [3-4]. Comparatively, polyimide has a higher surface tension than PDMS which indicates that polyimide is more hydrophilic than PDMS. As shown in Fig. 7(b), the three probe liquids, IPA, MMA and acetone were almost in perfect wetting conditions with polyimide in which the contact angles for the three liquids are nearly zero (or cos θ =1) but this was not found in the case of PDMS (Fig. 7(b)). In fact, the wettability of a surface can be simply judged by measuring the contact angle formed between distilled water and a surface. In this case, the contact angle formed between water-PDMS and water-polyimide is 88.14^o and 75.8^o, respectively. In other words, it shows that polyimide is more readily wet table by a fluid than PDMS but both are of high wettability for contact angles< 90^o. Hydrophilic is typically used to describe a property of a molecule and refers to the likelihood of its bonding with the hydrogen molecule in water [4-7]. Therefore, PDMS is more wet table by water than polyimide. In a hydrophobic interaction, what happened is that the water is rejected by the hydrophobic polyimide molecules in favour of bonding to itself [8].

4. Conclusion

An improved contact angle measurement tool and experimental setup to determine critical surface tension based on Fox-zisman's theory is presented this paper. The integrated system consists of simple apparatus and software which can be used to determine the critical surface tension of a substrate manually and automatically. This system is suitable for routine use. The surface tension determination method based on the contact angle measurements is essential because of a relative ease in performing measurements and it is able to provide high accuracy of measurements.

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